

crystals of a mineral somewhat resembling ottrelite have been developed; a conglomerate, the matrix of which is rather altered, as in the case of certain "Huronian" conglomerates, and a black-garnet micaceous schist, exactly resembling a rock which occurs in the Lepontine Alps at various localities from the neighbourhood of the Lukmanier Pass to the Binnental. Several of the schists resemble those which occur in the "upper schist" group (as defined by one of the authors) in the Alpine chain. Certain rather fine-grained speckled gneisses resemble a variety of that rock common in the Blair Athol district (Scotland).

Among the minerals or vein-specimens, the most interesting is one which presents some resemblance to jadeite. Microscopic examination shows it to consist of an aggregate of minute minerals, very difficult to distinguish, and chemical analysis suggests that the most probable are lime-garnet, jadeite, saussurite, or an allied mineral, and a pyroxene. As the specimen was collected from a moraine, its origin is conjectural, but that it was a vein-specimen seems most probable.

The minerals (among others) are actinolite, garnet, idocrase, noble serpentine, pyrite, and copper ores.

The geographical distribution of the rocks is described, and it is shown that in these mountains, as in the Alps, remnants of sedimentary rocks, probably of more than one geological era, are folded in among great masses of crystalline rocks, some, doubtless of igneous origin, but others metamorphosed sediments. It is evident that here, also, the rocks, as a rule, have been greatly modified by the effects of earth-movements.

#### V. "Contributions to the Chemistry of Chlorophyll. No. V."

By EDWARD SCHUNCK, F.R.S. Received February 15, 1894.

My previous papers were devoted to a description of various products derived from chlorophyll and their qualitative reactions. In the present communication I propose to give an account of some experiments made with a view to ascertain the composition of some of the derivatives of chlorophyll previously described.

Considerable difficulty was experienced in obtaining quantities of the various substances in a state sufficiently pure for analysis. This was especially the case with phyllocyanin and phylloxanthin, which, by the methods of purification employed so far, cannot be obtained entirely free from fatty matter. No attempt was therefore made to determine their composition. Of the compounds of phyllocyanin there is one, the phyllocyanin cupric acetate, which crystallises well, and has the appearance of a definite compound. Its composition was

accordingly determined, two analyses made by different observers leading to concordant results. Unfortunately, as previously explained, the compound is of such a nature as to make the elimination of copper and the consequent separation of the phyllocyanin impossible; otherwise the preparation of pure phyllocyanin from the compound would have been easy.

More satisfactory results were obtained in the case of phyllotaonin and its compounds. These beautiful substances being well crystallised and easily soluble in chloroform, but much less so in alcohol, may be obtained in a state of comparative purity, and I have reason to think that the numbers yielded by analysis represent, with tolerable accuracy, the composition of these bodies, although, in consequence of their high atomic weights, some doubt remains even as regards the corresponding empirical formulæ.

*Phyllocyanin Cupric Acetate.*

The preparation and properties of this compound have been previously described. Its analysis led to the following results.

I. 0.1221 gram substance gave 0.2715 CO <sub>2</sub> and 0.0577 H <sub>2</sub> O.				
0.4226	"	"	"	17.8 c.c. N at 15° and 728.6 mm.
0.2065	"	"	"	0.0236 CuO.
II. 0.4763 " " " 1.0550 CO <sub>2</sub> and 0.2315 H <sub>2</sub> O.				

These numbers correspond in 100 parts to

	I.	II.
C .....	60.64	60.40
H .....	5.25	5.39
N .....	4.74	—
Cu .....	9.12	9.07 *

The formula C<sub>67</sub>H<sub>71</sub>N<sub>5</sub>O<sub>7</sub>Cu<sub>2</sub> requires

C .....	60.27
H .....	5.33
N .....	4.49
Cu .....	9.52
O .....	20.39

*Methylphyllotaonin.*

The substance prepared in the manner formerly described, though apparently pure, was still contaminated with fatty matter, and had

\* The details of the analysis yielding this percentage of Cu are unfortunately lost.

to be recrystallised several times in order to get it into a state fit for analysis. This process of purification, as well as the subsequent determinations, were undertaken by Dr. L. Marchlewski, whose scrupulous care and manipulative skill afford a sufficient guarantee for the accuracy of the results obtained.

I think it unnecessary to give the details of analysis of more or less pure specimens of the substance, but I may state that the crystals when first prepared gave the following percentages of C, H, and N.

C	.....	70.27
H	.....	5.89
N	.....	9.89

The substance, after being purified by dissolving it in chloroform, adding a large quantity of alcohol, and collecting the crystals deposited on standing, the process being repeated three times, gave as the result of two determinations 11.93 and 11.85 per cent. nitrogen. After three further crystallisations the percentage of nitrogen was found to be 12.07 and 11.87. The four analyses agreeing so well as regards the nitrogen it was assumed that the substance was pure, and it only remained therefore to determine the C and H, the results obtained being as follows :

I.	0.1521	gram substance	gave	0.3838	CO <sub>2</sub>	and	0.0852	H <sub>2</sub> O.
II.	0.1877	"	"	"	0.4745	"	"	0.0998 "
III.	0.1284	"	"	"	0.3246	"	"	0.0683 "

In 100 parts

	I.	II.	III.
C	..... 68.71	68.82	68.94
H	..... 6.20	5.90	5.91

Taking the mean of the numbers given the composition of methylphyllotaonin would correspond to

C	.....	68.82
H	.....	6.00
N	.....	11.93
O	.....	13.25*

#### *Ethylphyllotaonin.*

In order to purify this substance the same method was adopted as in the case of methylphyllotaonin, *i.e.*, it was dissolved in chloroform

\* Some time ago Mr. Percy C. Bell, working with a less pure specimen of methylphyllotaonin, found it to contain in 100 parts—

C	.....	68.87
H	.....	6.46

and obtained in crystals on the addition to the solution of several times its volume of alcohol. After this process had been repeated several times two determinations yielded as a mean

C	.....	68·73
H	.....	5·87
N	.....	12·33

The substance having this composition was recrystallised four times in the same way as before, after which analysis led to the following results:—

- I. 0·1407 gram substance gave 0·3571 CO<sub>2</sub> and 0·0762 H<sub>2</sub>O.  
 II. 0·1020           ,,           ,,   0·2589 CO<sub>2</sub> and 0·0560 H<sub>2</sub>O.  
 III. 0·1002           ,,           ,,   0·01143 gram N.

In 100 parts

	I.	II.	III.
C	..... 69·22	69·22	—
H	..... 6·01	6·07	—
N	..... —	—	11·40

Want of material prevented further attempts at purification. It will be seen that methylphyllotaonin and ethylphyllotaonin approach each other very closely in composition, as they also do in appearance and general properties.

#### *Phyllotaonin.*

This substance was obtained by saponification in the manner formerly described, partly from methylphyllotaonin, partly from ethylphyllotaonin. After drying at 130° analysis yielded the following results:

- I. 0·1245 gram substance from methylphyllotaonin gave 0·3116 CO<sub>2</sub> and 0·0675 H<sub>2</sub>O,  
 II. 0·1921 gram substance from ethylphyllotaonin gave 0·4884 CO<sub>2</sub> and 0·1062 H<sub>2</sub>O.

In 100 parts

	I.	II.
C	..... 68·26	68·76
H	..... 6·02	6·14

Mr. W. Joseland made two analyses of phyllotaonin, the results being as follows:—

- I. 0·2076 gram substance gave 0·5239 CO<sub>2</sub> and 0·1093 H<sub>2</sub>O.  
 II. 0·2149 gram substance gave 24·10 c.c. N. at 22·5° and 951 mm.

In 100 parts

	I.	II.
C .....	68·82	68·61
H .....	5·85	5·88
N .....	12·85	—

*Phyllotaonin Acetate.*

This compound was prepared by dissolving phyllotaonin in boiling glacial acetic acid and allowing to crystallise.

0·1282 gram substance dried at 130° gave 0·3194 CO<sub>2</sub> and 0·0715 H<sub>2</sub>O.

In 100 parts

C .....	67·95
H .....	6·17

In determining the C and H of this compound, Mr. Joseland obtained the following numbers:—

0·1425 gram substance gave 0·3564 CO<sub>2</sub> and 0·0754 H<sub>2</sub>O.

In 100 parts

C .....	68·25
H .....	5·88

There are several formulæ with which the analyses of the derivatives of chlorophyll given above more or less closely agree, as will be seen from the following table:—

*Phyllotaonin.*

		Calculated.		
	Found.	C <sub>20</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> (OH).	C <sub>40</sub> H <sub>38</sub> N <sub>6</sub> O <sub>5</sub> (OH).	C <sub>41</sub> H <sub>41</sub> N <sub>6</sub> O <sub>5</sub> (OH).
C ....	68·51	68·57	68·67	68·90
H ....	6·08	5·71	5·58	5·88
N ....	12·85	12·00	12·00	11·76

*Methylphyllotaonin.*

		Calculated.		
	Found.	C <sub>20</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> (OCH <sub>3</sub> ).	C <sub>40</sub> H <sub>38</sub> N <sub>6</sub> O <sub>5</sub> (OCH <sub>3</sub> ).	C <sub>41</sub> H <sub>41</sub> N <sub>6</sub> O <sub>5</sub> (OCH <sub>3</sub> ).
C ....	68·82	69·23	69·00	69·23
H ....	6·00	6·04	5·74	6·04
N ....	11·92	11·54	11·77	11·53

## Ethylphyllotaonin.

		Calculated.		
		$C_{20}H_{19}N_3O_2(OC_2H_5)$ .	$C_{40}H_{38}N_6O_5(OC_2H_5)$ .	$C_{41}H_{41}N_6O_5(OC_2H_5)$ .
C ....	69.22	69.84	69.32	69.54
H ....	6.04	6.35	5.91	6.19
N ....	11.40	11.11	11.55	11.32

## Acetylphyllotaonin.

		Calculated.		
		$C_{20}H_{19}N_3O_5(OAc)$ .	$C_{40}H_{38}N_6O_5(OAc)$ .	$C_{41}H_{41}N_6O_5(OAc)$ .
C ....	67.95	67.34	68.01	68.25
H ....	6.17	5.61	5.53	5.82

VI. "Thermo-electric Properties of Salt Solutions." By GEORGE FREDERICK EMERY, B.A., LL.M., of the Inner Temple, late Scholar of Trinity College, Cambridge. Communicated by Professor J. J. THOMSON, F.R.S. Received February 8, 1894.

The thermo-electrical properties of solutions have not hitherto received much attention from physicists. If we form a circuit of two substances, one a metallic wire and the other a solution, and arrange it so that the junctions between the metal and the liquid are at different temperatures, we generally find that an electromotive force is developed in the circuit which varies in magnitude nearly in proportion to the difference of temperature between the junctions, and which, in comparison with the ordinary thermo-electromotive forces in metallic circuits, is very considerable. Up to the present time, as far as I am aware, the only extensive measurements of such thermo-electric forces are those of M. Bouty ('Journ. de Phys.,' vol. 9). He concludes that for a given difference of temperature between the junctions when the metal is constant the E.M.F. is nearly independent of the nature and strength of the solution (the solution being of some salt of the metal used).

The object of my experiments has been to see how far this is true, and to find out how (in the event of its not being strictly true) the E.M.F. varies with variations both in the strength and in the nature of the solution. The results show that both have considerable influence on the magnitude of the E.M.F.

My method of observation is as follows: the solution to be examined is put in a U-tube (fig. 1, A), in each limb of which is one of the ends of metal, which we may for convenience call electrodes, BB.